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- (71) Applicant (for all designated States except US): **CIBA
SPECIALTY CHEMICALS HOLDING INC.** [CH/CH];
Klybeckstrasse 141, CH-4057 Basel (CH).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **BOLLE, Thomas**
[DE/DE]; Bahnhofstrasse 3/2, 79588 Efringen-Kirchen
(DE). **REICHERT, Hans** [DE/DE]; Burstelstrasse 17,
79618 Rheinfelden (DE). **SIMMENDINGER, Peter**
[DE/CH]; Sandweg 8, CH-4123 Allschwil (CH).
- (74) Common Representative: **CIBA SPECIALTY CHEM-
ICALS HOLDING INC.**; Patent Department, Klybeck-
strasse 141, CH-4057 Basel (CH).
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(54) Title: METHOD OF PRINTING A TIME-TEMPERATURE INTEGRATOR ONTO A SUBSTRATE

(57) Abstract: The present invention relates to a method of printing a substrate, comprising (a) printing onto the substrate a time--
temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions.

Method of printing a time-temperature integrator onto a substrate

The present invention relates to a method of printing a substrate, comprising (a) printing onto the substrate a time-temperature integrator (TTI) which comprises at least one indicator having photochromic properties based on transfer reactions.

When perishable materials are used it is often desirable to ascertain the age and the current usable condition of the materials. While the application of an expiry date to the packaging was formerly considered sufficient, for a large number of products such a procedure is nowadays too inaccurate and insufficiently tamper-proof. In particular, the condition of perishable products is generally a function not only of time but also of other variables, such as, especially, temperature.

US-B-3,999,946 addresses this problem and proposes providing the perishable products with an indicator giving the time/temperature history. According to the length of storage and the storage temperature of the product, the originally colourless acetylene-based indicator exhibits a characteristic, irreversible colour change from which the quality of the stored perishable product can be inferred.

US-B-4,389,217 describes a time-temperature integrator consisting of two layers, each of which comprises a diacetylene material, the first layer comprising unreacted diacetylene material (= start time) and the second layer comprising partially reacted diacetylene material.

EP-A-117 390 describes a time-temperature integrator based on diacetylene materials, wherein the change in the reflectance of the diacetylene materials is measured and the diacetylene materials are applied to the substrate by means of customary printing techniques, such as flexographic printing, intaglio printing, screen printing, ink-jet printing or letterpress printing.

US-B-5,057,434 describes a time-temperature integrator which consists of at least two functional layers. One layer can be, for example, a diacetylene material that expires after 21 days at 3.3°C. The second layer consists of a material having a melting point above 6°C and a dye. At temperatures above 6°C, the dye becomes mobile in the second layer, that is to say it diffuses through the layers and makes an additive colour contribution to the indicator. This system makes it possible, on the one hand, to monitor the shelf life of the

foodstuff and, on the other hand, to indicate storage at too high a temperature. The layers are preferably applied by means of customary printing techniques.

An obstacle to widespread use of the methods known from US-B-3,999,946, US-B-4,389,217, EP-A-117 390 and US-B-5,057,434 is their inconvenient handling. For example, the indicator has to be stored in the dark at very low temperatures until it is applied to the product in order initially to delay the onset of the time-temperature effect actually desired, which is initiated on synthesis of the indicator. The indicator reaction itself takes place autocatalytically and is highly non-linear, which renders precise evaluation more difficult.

US-B-5,053,339 (WO 92/09870) describes a time-temperature integrator (TTI) which consists of a layer comprising the indicator, a barrier layer that is impermeable to the indicator and permeable to the activator, and a layer comprising the activator. In dependence upon the temperature, the activator diffuses through the barrier layer into the indicator layer, where it provides a change in colour.

WO 99/39197 relates to a substrate for the packaging of, or for application to, ageing- and temperature-sensitive products, the substrate having, arranged in the region of the substrate, a planar time-temperature integrator comprising a matrix and at least one reversible indicator embedded therein, the indicator having photochromic properties based on transfer reactions. The nature and the amount of the TTI used for printing can be matched to the perishable products. Furthermore, the TTI can be used in the form of a solution and/or in the form of an aqueous dispersion.

Starting from that prior art, the problem underlying the invention is to provide a method which enables the quality of the products to be determined and which is simple to handle.

The problem according to the invention is solved by a method of determining the quality of ageing- and temperature-sensitive products, which comprises the following steps:

- a) printing onto a substrate a time-temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined below,
- b) activation, especially photo-induced coloration, of the indicator,
- c) optionally application of a protector which prevents renewed photo-induced coloration of the indicator, and

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d) determination of the degree of time- or temperature-induced decoloration and, taking account of the degree of decoloration, the quality of the product; or by a method of printing a substrate, comprising
(a) printing onto the substrate a time-temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions.

A transfer reaction is generally to be understood as being a reaction which includes a change in the atomic connectivities, the rearrangement of at least one atom being involved. An example thereof is the transfer of a hydrogen atom (or a proton or hydride). In that case the above-mentioned species is transferred from a "donor" group to an "acceptor" group and in so doing forms a tautomeric compound. When other groups are transferred, isomeric or charged species may be formed in the transfer reaction.

By virtue of its photochromic properties, the indicator can undergo photo-induced coloration by irradiation with photons of a specific energy range, the coloration being followed by a time- and temperature-dependent decoloration. The coloration of the indicator can take place at a defined timepoint, preferably, for example, immediately after printing of the substrate, which is especially the packaging of a perishable material.

The time-temperature clock can accordingly be started at a defined desired timepoint and does not begin to run irreversibly at the time of the indicator synthesis. Decoloration is preferred for consideration according to the invention, but the use of an indicator in which the coloration process forms the basis of the time-temperature clock is also conceivable.

After printing and activation, the time-temperature integrator is, if necessary, provided with a protector which prevents the renewed photo-induced coloration of the reversible indicator. Such a protector may be a protective coating (overprint varnish) or a laminate that comprises a filter which, by filtering out certain wavelength ranges, is intended to prevent undesirable renewed coloration of the indicator after the time-temperature clock has started.

In addition, for the purpose of tamper-proofing, it is possible for a further, irreversible indicator to be arranged e.g. alongside or over the reversible indicator. The further indicator indicates by means of an irreversible colour change that the reversible indicator has undergone renewed coloration after production or packaging of the perishable goods.

It is also possible to produce indicators having more than one characteristic time domain. Such indicators can have, for example, a phase transition, with the different phases exhibiting different decoloration behaviours. The simultaneous use of two or more indicators having different time domains is likewise possible; that is to say it is possible to use, for example, two or more indicators of formulae I to VI, optionally in combination with other indicators, for example those indicating storage of the perishable product at too high a temperature.

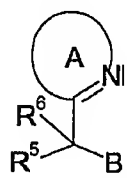
The actual determination of the quality of ageing- or temperature-sensitive products is preceded by the photo-induced coloration of the reversible indicator. The coloration is effected prior to the application of a filter or of the irreversible indicator. At a later timepoint, the degree of time- or temperature-induced decoloration is then measured and the quality of the product is inferred therefrom. When an evaluation is made with the aid of the human eye, it may be advantageous to arrange e.g. alongside or below the substrate a reference scale which allocates a certain quality grade, a certain timepoint *etc.* to a certain degree of decoloration.

The method according to the invention is suitable for marking perishable products such as foodstuffs (e.g. frozen foods), medicaments, drugs, transplant organs and perishable raw materials.

The photochromic indicator reactions can be based, for example, on reversible electron transfer or on the reversible transfer of a charged or uncharged hydrogen atom (proton, hydride) or a hydrogen isotope (deuterium, tritium). Preference is given to the transfer of protons, deuterons, halogen radical ions or simple chemical groups, such as methyl groups.

It is generally the case that, depending upon the nature of the photochemically induced transfer reaction and especially according to the binding strength of the "acceptor" of the transferred species, it is possible to achieve different lengths of decoloration time.

Examples of indicators are compounds of the general formula

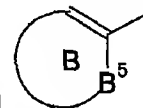


, wherein B is an electron-attracting group, such as a nitrile group, an ester group (-C(=O)OEt), a carboxylic acid group, an aldehyde group (-C(=O)H), a keto group, a fully or

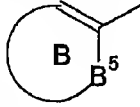
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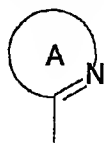
partially halogenated alkyl radical, such as a trifluoromethyl group, a halogen atom, a nitro

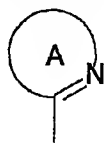
group, a group $-\text{PPh}_3^+ \text{X}^-$, wherein X^- is an anion, such as Cl^- , or a radical



, the

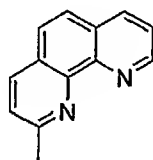
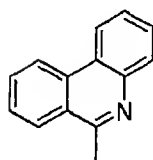
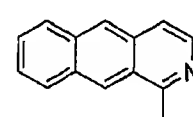
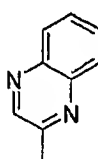
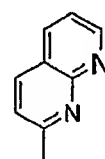
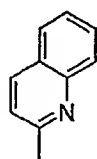
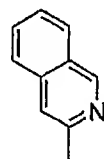
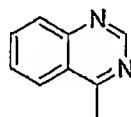
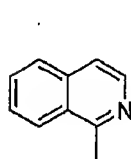
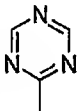
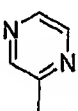
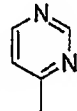
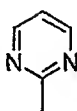
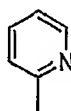
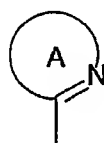
radical  being a $\text{C}_6\text{-C}_{30}$ aryl radical or $\text{C}_2\text{-C}_{30}$ heteroaryl radical, which can be unsubstituted or substituted,



the radical  is a $\text{C}_2\text{-C}_{30}$ heteroaryl radical, which can be unsubstituted or substituted, and B^5 , R^5 and R^6 are as defined below.

Examples of the radical

are

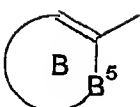
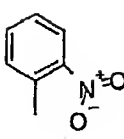
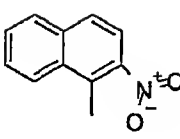
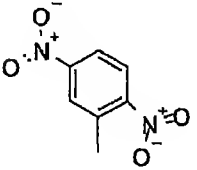


and

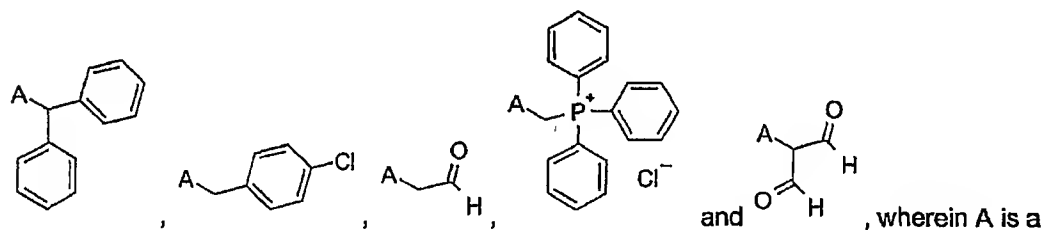
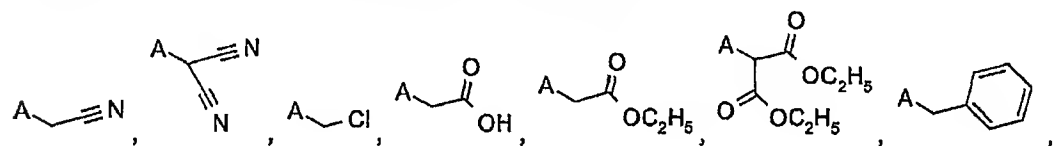
, which can have one or more substituents from the group

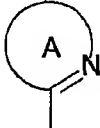
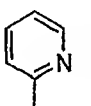
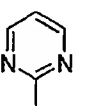
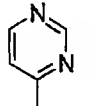
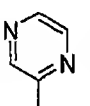
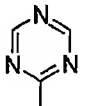
fluorine atom, chlorine atom, bromine atom, C_{1-18} alkyl radical, especially C_{1-4} alkyl radical, and $\text{C}_6\text{-C}_{14}$ aryl radical, especially phenyl group.

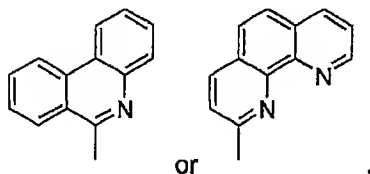
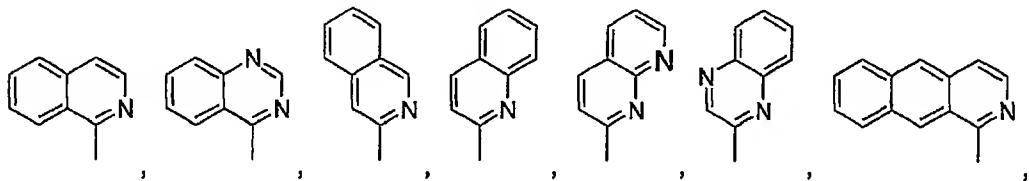
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Examples of the radical  are ,  and , which can have one or more substituents from the group fluorine atom, chlorine atom, bromine atom, C₁₋₁₈alkyl radical, especially C₁₋₄alkyl radical, and C₆₋₁₄aryl radical, especially phenyl group.

Examples in which B is not a ring system are listed below:

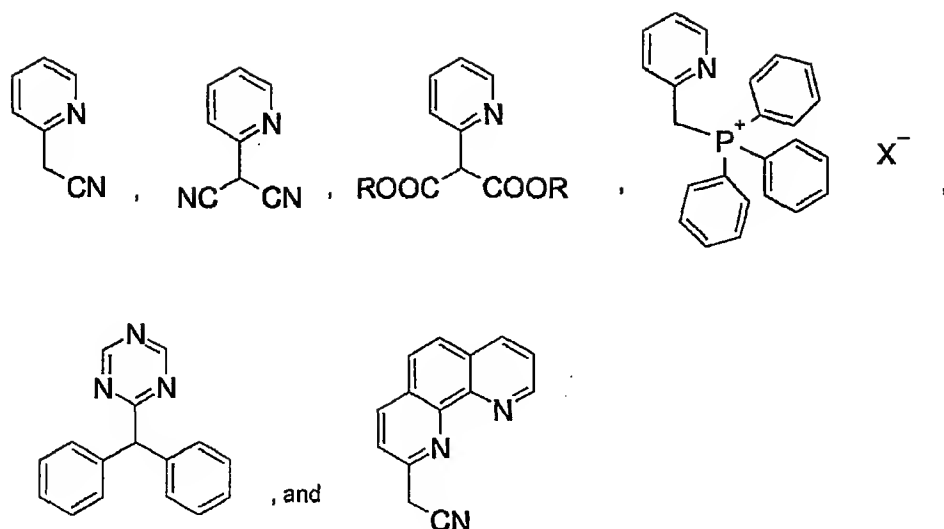


radical , especially a group of formula , , , , ,



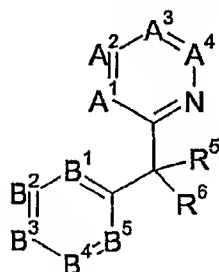
More specifically, examples in which B is not a ring system include:

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wherein R is a C₁₋₁₈alkyl radical.

Preferred as reversible indicators are compounds of general formula



(I), wherein

A¹ is a nitrogen atom or a group C-R¹,

A² is a nitrogen atom or a group C-R²,

A³ is a nitrogen atom or a group C-R³,

A⁴ is a nitrogen atom or a group C-R⁴, wherein

R¹, R², R³ and R⁴ are each independently of the others a hydrogen atom, an isotope thereof or a fluorine atom, a chlorine atom, a bromine atom, a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, or a C₆-C₁₄aryl radical, especially a phenyl group,

R⁵ is a hydrogen atom, an isotope thereof (D or T), a nitrile group, an ester group, an aldehyde group, a carboxylic acid group, a keto group, a fluorine atom, a chlorine atom, a bromine atom or a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, a C₆-C₁₄aryl radical, especially an unsubstituted or substituted phenyl group, or a C₂-C₁₃heteroaryl radical, especially an unsubstituted or substituted pyridine group,

R⁶ is a hydrogen atom (H) or an isotope thereof (D or T),

B¹ is a nitrogen atom or a group C-R⁷,

B² is a nitrogen atom or a group C-R⁸,

B³ is a nitrogen atom or a group C-R⁹,

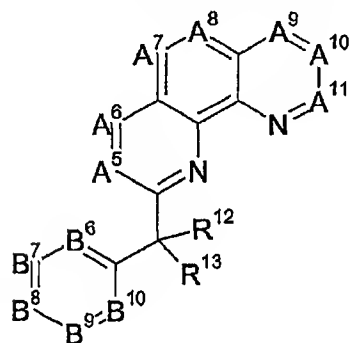
B⁴ is a nitrogen atom or a group C-R¹⁰,

B⁵ is a nitrogen atom or a group C-R¹¹, wherein

R⁷, R⁸, R⁹ and R¹⁰ are each independently of the others a hydrogen atom, an isotope thereof or a fluorine atom, a chlorine atom, a bromine atom or a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, or a C₆-C₁₄aryl radical, especially a phenyl group, and

R¹¹ is a nitro group, a cyano group, a carboxylic acid group or a derivative thereof, such as a carboxylic acid ester group or a carboxylic acid amide group, a ketone group or an aldehyde group;

compounds of general formula



(II), wherein

A⁵ is a nitrogen atom or a group C-R¹⁴,

A⁶ is a nitrogen atom or a group C-R¹⁵,

A⁷ is a nitrogen atom or a group C-R¹⁶,

A⁸ is a nitrogen atom or a group C-R¹⁷,

A⁹ is a nitrogen atom or a group C-R¹⁸,

A¹⁰ is a nitrogen atom or a group C-R¹⁹,

A¹¹ is a nitrogen atom or a group C-R²⁰, wherein

R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹ and R²⁰ are each independently of the others a hydrogen atom, an isotope thereof, a fluorine atom, a chlorine atom, a bromine atom, a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, or a C₆-C₁₄aryl radical, especially a phenyl group,

R¹² is a hydrogen atom, an isotope thereof (D or T), a nitrile group, an ester group, an aldehyde group, a carboxylic acid group, a keto group, a fluorine atom, a chlorine atom, a bromine atom or a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, a C₆-C₁₄aryl radical, especially an unsubstituted or substituted phenyl group, or a C₂-C₁₃heteroaryl radical, especially an unsubstituted or substituted pyridine group,

R¹³ is a hydrogen atom (H) or an isotope thereof (D or T),

B⁶ is a group C-R²¹,

B^7 is a group $C-R^{22}$,

B^8 is a group $C-R^{23}$,

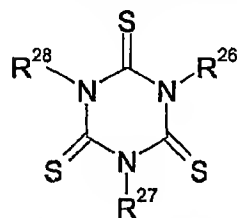
B^9 is a group $C-R^{24}$,

B^{10} is a group $C-R^{25}$, wherein

R^{21} , R^{22} , R^{23} and R^{24} are each independently of the others a hydrogen atom, an isotope thereof or a fluorine atom, a chlorine atom, a bromine atom or a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, or a C_6-C_{14} aryl radical, especially a phenyl group, and

R^{25} is a nitro group, a cyano group, a carboxylic acid group or a derivative thereof, such as a carboxylic acid ester group or a carboxylic acid amide group, a ketone group or an aldehyde group;

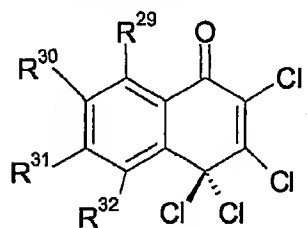
compounds of general formula



(III), wherein

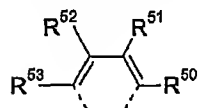
R^{26} , R^{27} and R^{28} are each independently of the others a C_{1-6} alkyl radical, especially a methyl or ethyl group;

compounds of general formula



(IV), wherein

R^{29} , R^{30} , R^{31} and R^{32} are each independently of the others a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, or a C_6-C_{14} aryl radical, especially a phenyl group; or two of the radicals R^{29} , R^{30} , R^{31} and R^{32} together form a group of the formula

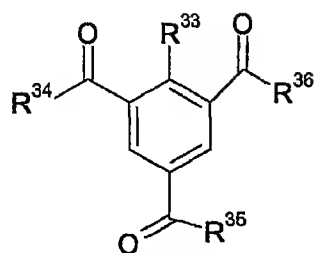


, wherein

R^{50} , R^{51} , R^{52} and R^{53} are each independently of the others H, a C_1-C_{18} alkyl radical or a C_6-C_{18} aryl radical, which can be unsubstituted or substituted;

compounds of general formula

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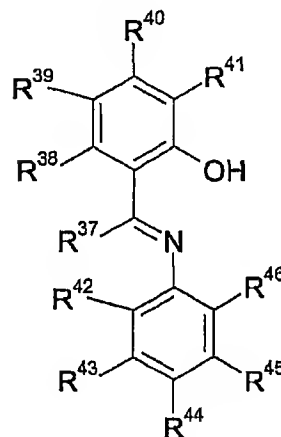


(V), wherein

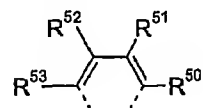
 R^{33} is a C_{1-18} alkyl radical, R^{34} , R^{35} and R^{36} are each independently of the others a hydrogen atom or a C_{1-18} alkyl radical;

or

compounds of general formula



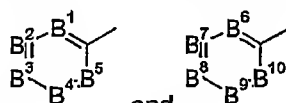
(VI), wherein

 R^{37} is a hydrogen atom or a C_{1-18} alkyl radical, and R^{38} , R^{39} , R^{40} , R^{41} , R^{42} , R^{43} , R^{44} , R^{45} and R^{46} are each independently of the others a hydrogen atom, a C_{1-18} alkyl radical or a C_{1-18} alkoxy radical, ortwo of the radicals R^{38} , R^{39} , R^{40} , R^{41} , R^{42} , R^{43} , R^{44} , R^{45} and R^{46} together form a group of the formula

, wherein

 R^{50} , R^{51} , R^{52} and R^{53} are each independently of the others H, a C_1 - C_{18} alkyl radical or a C_6 - C_{18} aryl radical, which can be unsubstituted or substituted.

Of the compounds of formulae I to VI mentioned above, preference is given to those of

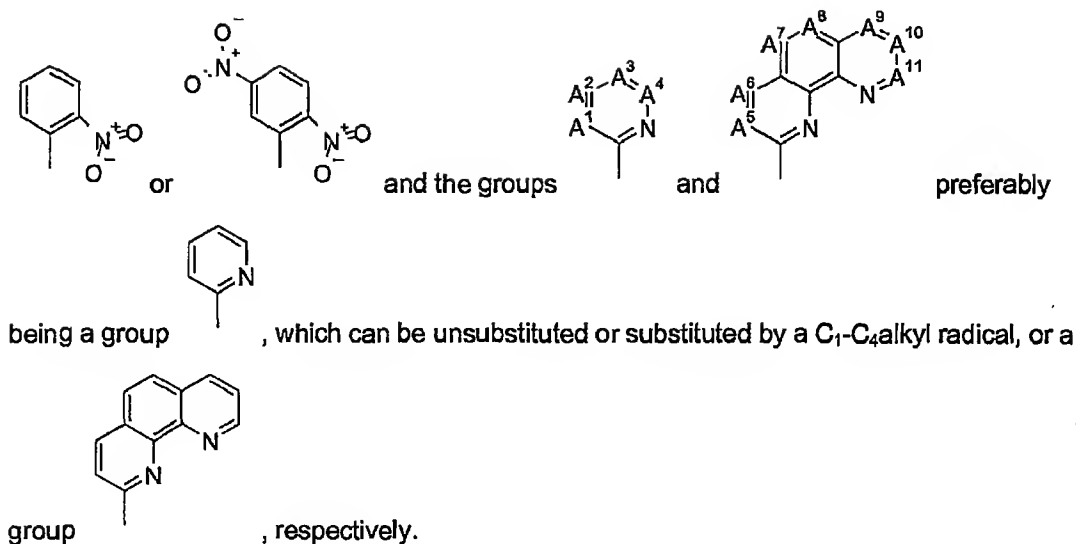


formulae I and II, the groups

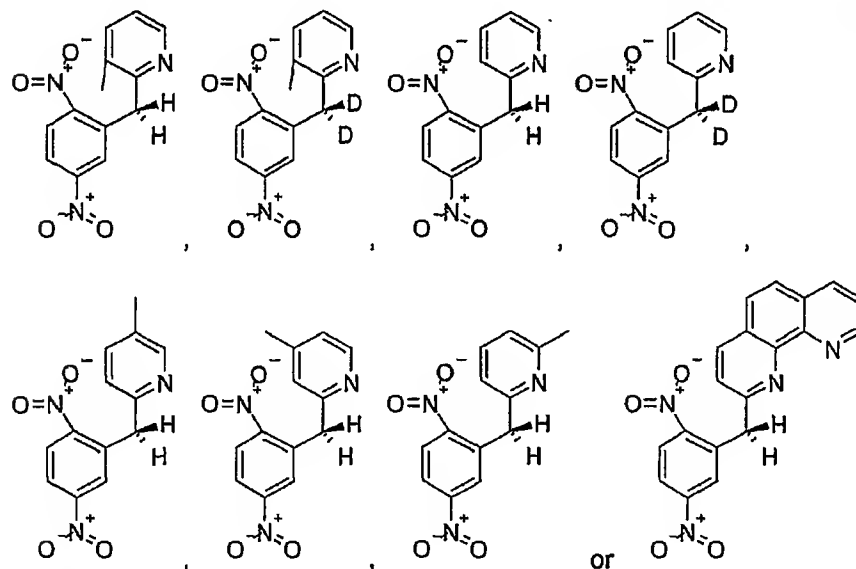
and

preferably being a group

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The reversible indicator is more especially a compound of general formula I or II, namely

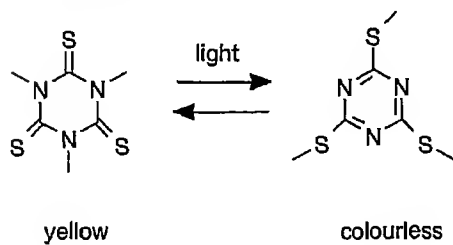
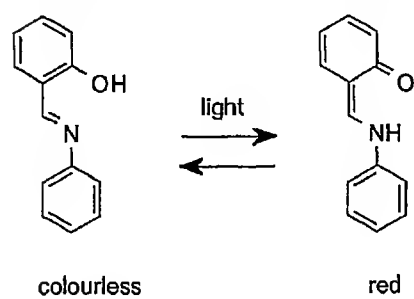
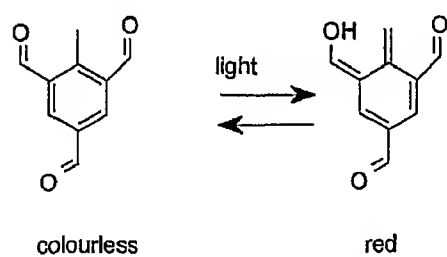
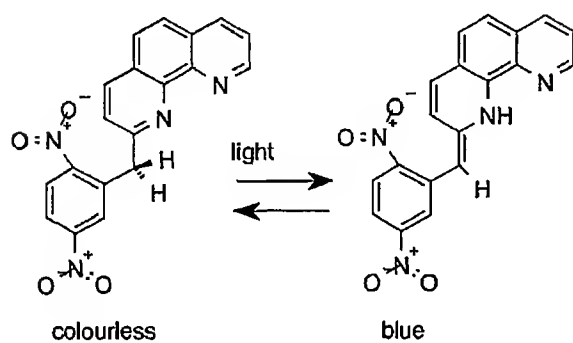
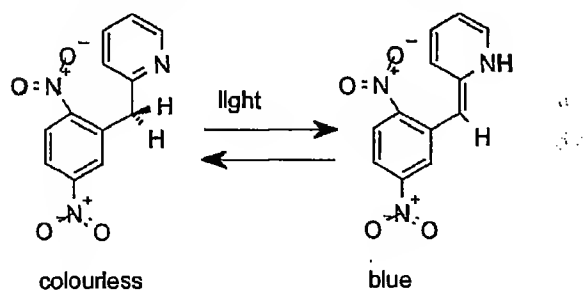


Depending upon the application, a compound having optimised time-temperature behaviour can be used.

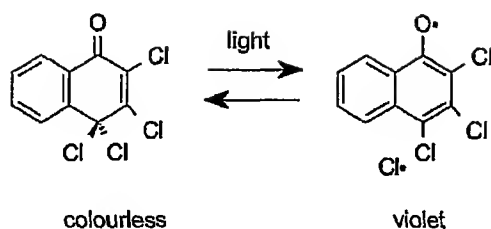
Proton transfer reactions are shown diagrammatically by way of example below. In such reactions, the initially colourless indicator is irradiated with UV light or near-UV light, where-upon a proton transfer and an associated indicator coloration take place. Such a photo-induced proton transfer then proceeds as a function of time and temperature in the other direction again, so that the indicator is successively decolorised. Analogous reactions, based

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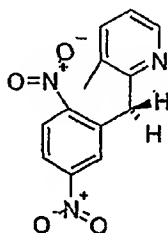
on the transfer of methyl groups or halogen radicals, are likewise shown.



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A compound having two crystalline phases and two different characteristic time domains is described below. At a temperature of 318 K, a phase transfer takes place from a first crystalline phase having long decoloration times to a second crystalline phase having a decoloration time that is shorter by a factor of 10.



The term "halogen atom" denotes an iodine atom, a fluorine atom, a bromine atom or a chlorine atom, preferably a fluorine atom, a bromine atom or a chlorine atom.

C₁-C₄Alkyl denotes methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl or tert-butyl; C₁-C₈alkyl denotes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-amyl, tert-amyl or hexyl; C₁-C₁₈alkyl denotes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-amyl, tert-amyl, hexyl, heptyl, octyl, 2-ethylhexyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl.

The "C₆-C₃₀aryl radical" is typically a C₆-C₂₄aryl radical, such as phenyl, indenyl, azulenyl, naphthyl, biphenyl, as-indacenyl, s-indacenyl, acenaphthylenyl, phenanthryl, fluoranthenyl, triphenylenyl, chrysenyl, naphthacenyl, picenyl, perylenyl, pentaphenyl, hexacenyl, pyrenyl or anthryl, preferably phenyl, 1-naphthyl, 2-naphthyl, 9-phenanthryl, 2- or 9-fluorenyl, 3- or 4-biphenyl, which can be unsubstituted or substituted. Examples of C₆-C₁₄aryl are phenyl, 1-naphthyl, 2-naphthyl, 3- or 4-biphenyl, which can be unsubstituted or substituted.

The "C₂-C₃₀heteroaryl radical" is a ring or ring system in which O, S or N are possible hetero atoms and is typically an unsaturated heterocyclic radical having from 5 to 30 atoms, which has at least 6 conjugated π -electrons, such as thienyl, benzo[b]thienyl, dibenzo[b,d]thienyl,

thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, 2H-chromenyl, xanthenyl, dibenzofuranyl, phenoxythienyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, 1H-pyrroliziny, isoindolyl, pyridazinyl, indoliziny, isoindolyl, indolyl, 3H-indolyl, phthalazinyl, naphthyridinyl, quinoxaliny, quinazolinyl, cinnoliny, indazolyl, purinyl, quinoliziny, quinolyl, isoquinolyl, phthalazinyl, naphthyridinyl, pteridinyl, carbazolyl, 4aH-carbazolyl, carbolinyl, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl or phenoxazinyl, preferably the above-mentioned mono- or bi-cyclic heterocyclic radicals, which can be unsubstituted or substituted.

The above-mentioned groups can be substituted, for example, by a C₁-C₈alkyl radical, a hydroxyl group, a mercapto group, a C₁-C₈alkoxy radical, a C₁-C₈alkylthio radical, a halogen atom, a halo-C₁-C₈alkyl radical, a cyano group, an aldehyde group, a ketone group, a carboxyl group, an ester group, a carbamoyl radical, an amino group or a nitro group.

The "carbamoyl radical" is typically a C₁₋₁₈carbamoyl radical, preferably a C₁₋₈carbamoyl radical, which can be unsubstituted or substituted, for example carbamoyl, methylcarbamoyl, ethylcarbamoyl, n-butylcarbamoyl, tert-butylcarbamoyl, dimethylcarbamoyloxy, morpholino-carbamoyl or pyrrolidinocarbamoyl.

Examples of a C₇-C₁₂aralkyl radical are benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl or ω,ω-dimethyl-ω-phenyl-butyl, it being possible for both the alkyl moiety and the aryl moiety to be unsubstituted or substituted.

The term "halo-C₁-C₈alkyl radical" denotes alkyl radicals in which some or all of the hydrogen atoms have been replaced by halogen atoms, such as, for example, a trifluoromethyl group *etc.* The "aldehyde group, ketone group and ester group" include those groups which can be substituted by a C₁-C₁₈alkyl radical, a C₆-C₁₄aryl radical or a C₇-C₁₂aralkyl radical, it being possible for the aryl radical and the aralkyl radical to be unsubstituted or substituted.

The printing inks according to the invention comprise the indicators, especially the compounds of formulae I, II, III, IV, V and VI, advantageously in a concentration of from 0.01 to 75 % by weight, preferably from 1 to 50 % by weight, especially from 5 to 40 % by weight, more especially from 10 to 25 % by weight, based on the total weight of the printing ink, and can be used, for example, for electrophotography, intaglio printing, flexographic printing, screen printing, offset printing or letterpress printing.

The printing ink is, for example, a liquid or paste-form dispersion comprising colorant (indicator), binder and optionally solvent and/or optionally water and additives. In a liquid printing ink, the binder and, where applicable, the additives are generally dissolved in a solvent. Customary viscosities in the Brookfield viscometer are, for example, from 20 to 5000 mPa·s, for example from 20 to 1000 mPa·s, for liquid printing inks. For paste-form printing inks, the values range, for example, from 1 to 100 Pa·s, preferably from 5 to 50 Pa·s. The person skilled in the art will be familiar with the ingredients and compositions of printing inks.

The printing inks can be used, for example, for electrophotography, intaglio printing, flexographic printing, screen printing, offset printing, lithography or letterpress printing. Suitable printing inks are both solvent-based printing inks and water-based printing inks. Of interest are, for example, printing inks based on aqueous acrylates. Such inks are to be understood as including polymers or copolymers that are obtained by polymerisation of at

least one monomer containing a group $\text{H}_2\text{C}=\text{C}(\text{O}-\text{O}-\text{---})$ or $\text{H}_2\text{C}=\text{C}(\text{O}-\text{N}-\text{---})$ and that are dissolved in

water or a water-containing organic solvent. Suitable organic solvents are water-miscible solvents customarily used by the person skilled in the art, for example alcohols, such as methanol, ethanol and isomers of propanol, butanol and pentanol, ethylene glycol and ethers thereof, such as ethylene glycol methyl ether and ethylene glycol ethyl ether, and ketones, such as acetone, ethyl methyl ketone or cyclohexanone, for example isopropanol. Water and alcohols are preferred.

Suitable printing inks comprise, for example, as binder primarily an acrylate polymer or copolymer and the solvent is selected, for example, from the group consisting of water, C₁-C₅alcohols, ethylene glycol, 2-(C₁-C₅alkoxy)-ethanol, acetone, ethyl methyl ketone and any mixtures thereof.

In addition to the binder, the printing inks may also comprise customary additives known to the person skilled in the art in customary concentrations.

For intaglio or flexographic printing, a printing ink is usually prepared by dilution of a printing ink concentrate and can then be used in accordance with methods known *per se*.

The printing inks may, for example, also comprise alkyd systems that dry oxidatively.

The printing inks are dried in a known manner customary in the art, optionally with heating of the coating.

A suitable aqueous printing ink composition comprises, for example, an indicator, a dispersant and a binder.

Dispersants that come into consideration include, for example, customary dispersants, such as water-soluble dispersants based on one or more arylsulfonic acid/formaldehyde condensation products or on one or more water-soluble oxalkylated phenols, non-ionic dispersants or polymeric acids.

The arylsulfonic acid/formaldehyde condensation products are obtainable, for example, by sulfonation of aromatic compounds, such as naphthalene itself or naphthalene-containing mixtures, and subsequent condensation of the resulting arylsulfonic acids with formaldehyde. Such dispersants are known and are described, for example, in US-A-5,186,846 und DE-A-197 27 767. Suitable oxalkylated phenols are likewise known and are described, for example, in US-A-4,218,218 und DE-A-197 27 767. Suitable non-ionic dispersants are, for example, alkylene oxide adducts, polymerisation products of vinylpyrrolidone, vinyl acetate or vinyl alcohol and co- or ter-polymers of vinyl pyrrolidone with vinyl acetate and/or vinyl alcohol. It is also possible, for example, to use polymeric acids which act both as dispersants and as binders.

Examples of suitable binder components that may be mentioned include acrylate-group-containing, vinyl-group-containing and/or epoxy-group-containing monomers, prepolymers and polymers and mixtures thereof. Further examples are melamine acrylates and silicone acrylates. The acrylate compounds may also be non-ionically modified (e.g. provided with amino groups) or ionically modified (e.g. provided with acid groups or ammonium groups) and used in the form of aqueous dispersions or emulsions (e.g. EP-A-704 469, EP-A-12 339). Furthermore, in order to obtain the desired viscosity, the solventless acrylate polymers can be mixed with so-called reactive diluents, for example vinyl-group-containing monomers. Further suitable binder components are epoxy-group-containing compounds.

The printing ink compositions may also comprise as additional component, for example, an agent having a water-retaining action (humectant), e.g. polyhydric alcohols, polyalkylene glycols, which renders the compositions especially suitable for ink-jet printing.

It will be understood that the printing inks may comprise further auxiliaries, such as are customary in the printing and coating industries, for example preservatives (such as glutaric dialdehyde and/or tetramethylolacetyleneurea, anti-oxidants, degassers/defoamers, viscosity regulators, flow improvers, anti-settling agents, gloss improvers, lubricants, adhesion promoters, anti-skin agents, matting agents, emulsifiers, stabilisers, hydrophobic agents, light stabilisers, handle improvers and anti-statics. When such agents are present

in the compositions, their total amount is generally ≤ 1 % by weight, based on the weight of the preparation.

The printing inks may also, for example, comprise solubilisers, e.g. ϵ -caprolactam.

The printing inks may, *inter alia* for the purpose of adjusting the viscosity, comprise thickeners of natural or synthetic origin. Examples of thickeners include commercially available alginate thickeners, starch ethers or locust bean flour ethers. The printing inks comprise such thickeners e.g. in an amount of from 0.01 to 2 % by weight, based on the total weight of the printing ink.

It is also possible for the printing inks to comprise buffer substances, for example borax, borate, phosphate, polyphosphate or citrate, in amounts of e.g. from 0.1 to 3 % by weight, in order to establish a pH value of e.g. from 4 to 9, especially from 5 to 8.5.

As further additives, such printing inks may comprise surfactants or humectants. Surfactants that come into consideration include commercially available anionic and non-ionic surfactants. Humectants that come into consideration include, for example, urea or a mixture of sodium lactate (advantageously in the form of a 50 to 60 % aqueous solution) and glycerol and/or propylene glycol in amounts of e.g. from 0.1 to 30 % by weight, especially from 2 to 30 % by weight, in the printing inks.

Furthermore, the printing inks may also comprise customary additives, for example foam-reducing agents or especially substances that inhibit the growth of fungi and/or bacteria. Such additives are usually used in amounts of from 0.01 to 1 % by weight, based on the total weight of the printing ink.

The printing inks may also be prepared in customary manner by mixing the individual components together, for example in the desired amount of water.

As already mentioned, depending upon the nature of the use, it may be necessary for e.g. the viscosity or other physical properties of the printing ink, especially those properties which influence the affinity of the printing ink for the substrate in question, to be adapted accordingly.

Substrate materials that may be mentioned include, for example:

- cellulosic materials, such as paper, paperboard, cardboard, which may also be varnished or have some other coating,
- metallic materials, such as foils, sheets or workpieces of aluminium, iron, copper, silver, gold, zinc or alloys of those metals, which may be varnished or have some other coating,
- silicate materials, such as glass, china and ceramics, which may likewise be coated,

- polymeric materials of all kinds, such as polystyrene, polyamides, polyester, polyethylene, polypropylene, melamine resins, polyacrylates, polyacrylonitrile, polyurethanes, polycarbonates, polyvinyl chloride and corresponding copolymers and block copolymers,
- textile materials, knitted goods, woven goods, non-wovens and made-up goods of polyester, modified polyester, polyester blends, cellulosic materials, such as cotton, cotton blends, jute, flax, hemp and ramie, viscose, wool, silk, polyamide, polyamide blends, polyacrylonitrile, triacetate, acetate, polycarbonate, polypropylene, polyvinyl chloride, polyester microfibres and glass fibre fabrics,
- foodstuffs and cosmetics.

Especially suitable substrates are e.g. paper, coated paper, cardboard and plastic or metal foils, such as aluminium foils.

Preference is given to printing processes wherein aqueous printing inks are used.

The printing of the substrate is preferably effected by means of continuous or dropwise ink-jet printing. The present invention relates also to non-aqueous or aqueous ink-jet inks which comprise a time-temperature integrator comprising at least one reversible indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined above. Aqueous ink-jet inks are preferred.

The inks may be non-aqueous inks which consist of a solution of the TTI in an organic solvent or a mixture of organic solvents. Examples of solvents that can be used for this purpose are alkyl carbitols, alkyl cellosolves, dialkylformamides, dialkylacetamides, alcohols, acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, diisopropyl ketone, dibutyl ketone, dioxane, ethyl butyrate, ethyl isovalerate, diethyl malonate, diethyl succinate, butyl acetate, triethyl phosphate, ethyl glycol acetate, toluene, xylene, Tetralin or petroleum ether fractions. Examples of solid waxes as solvents that, as ink vehicles, have to be heated first, are stearic or palmitic acid.

The inks preferably comprise a total content of indicators of from 1 to 35 % by weight, especially from 1 to 30 % by weight and preferably from 1 to 20 % by weight, based on the total weight of the ink. As lower limit, a limit of 1.5 % by weight, especially 2 % by weight and more especially 3 % by weight, is preferred.

The inks may comprise water-miscible organic solvents, for example C₁-C₄alcohols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol or iso-

butanol; amides, e.g. dimethylformamide or dimethylacetamide; ketones or ketone alcohols, e.g. acetone, diacetone alcohol; ethers, e.g. tetrahydrofuran or dioxane; nitrogen-containing heterocyclic compounds, e.g. N-methyl-2-pyrrolidone or 1,3-dimethyl-2-imidazolidone, polyalkylene glycols, e.g. polyethylene glycol, or polypropylene glycol; C₂-C₈alkylene glycols and thioglycols, e.g. ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, thiodiglycol, hexylene glycol and diethylene glycol; further polyols, e.g. glycerol or 1,2,6-hexanetriol; and C₁-C₄alkyl ethers of polyvalent alcohols, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol or 2-[2-(2-ethoxyethoxy)ethoxy]ethanol; preferably N-methyl-2-pyrrolidone, diethylene glycol, glycerol or especially 1,2-propylene glycol, usually in an amount of from 2 to 30 % by weight, especially from 5 to 30 % by weight and preferably from 10 to 25 % by weight, based on the total weight of the ink.

The inks may also comprise solubilisers, e.g. ϵ -caprolactam.

The printing inks may, *inter alia* for the purpose of adjusting the viscosity, comprise thickeners of natural or synthetic origin.

Furthermore, the pigment preparations according to the invention, especially when binder curing is to be effected by means of UV radiation, may comprise a photoinitiator which initiates the polymerisation.

Suitable photoinitiators for free radical photopolymerisations, that is to say the polymerisation of acrylates and, if desired, vinyl compounds, are e.g. benzophenone and benzophenone derivatives, such as 4-phenylbenzophenone and 4-chlorobenzophenone, acetophenone derivatives, such as 1-benzoylcyclohexan-1-ol, 2-hydroxy-2,2-dimethylacetophenone and 2,2-dimethoxy-2-phenylacetophenone, benzoin and benzoin ethers, such as methyl, ethyl and butyl benzoin ethers, benzil ketals, such as benzil dimethyl ketal, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, acylphosphine oxides, such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide and bisacylphosphine oxides.

Suitable photoinitiators for cationic photopolymerisations, that is to say the polymerisation of vinyl compounds or epoxy-group-containing compounds, are, for example, aryldiazonium salts, such as 4-methoxybenzenediazonium hexafluorophosphate, benzenediazonium tetrafluoroborate and toluenediazonium tetrafluoroarsenate, arylodonium salts, such as diphenyliodonium hexafluoroarsenate, arylsulfonium salts, such as triphenylsulfonium hexafluorophosphate, benzene- and toluene-sulfonium hexafluorophosphate and bis[4-diphenylsulfonio-phenyl]sulfide-bis-hexafluorophosphate, disulfones, such as diphenyl

disulfone and phenyl-4-tolyl disulfone, diazodisulfones, imidotriflates, benzoin tosylates, isoquinolinium salts, such as N-ethoxyisoquinolinium hexafluorophosphate, phenylpyridinium salts, such as N-ethoxy-4-phenylpyridinium hexafluorophosphate, picolinium salts, such as N-ethoxy-2-picolinium hexafluorophosphate, ferrocenium salts, and titanocenes.

When a photoinitiator is present in the ink compositions according to the invention, which is generally necessary for binder curing by UV radiation, the content thereof is generally from 0.1 to 10 % by weight, preferably from 0.1 to 8 % by weight.

Examples of thickeners that may be mentioned include commercially available alginate thickeners, starch ethers or locust bean flour ethers, especially sodium alginate on its own or in admixture with modified cellulose, for example methyl-, ethyl-, carboxymethyl-, hydroxyethyl-, methylhydroxyethyl-, hydroxypropyl- or hydroxypropylmethyl-cellulose, especially having preferably from 20 to 25 % by weight carboxymethylcellulose. Synthetic thickeners that may be mentioned are, for example, those based on poly(meth)acrylic acids or poly(meth)acrylamides.

The inks comprise such thickeners e.g. in an amount of from 0.01 to 2 % by weight, especially from 0.01 to 1 % by weight and preferably from 0.01 to 0.5 % by weight, based on the total weight of the ink.

It is also possible for the inks to comprise buffer substances, for example borax, borate, phosphate, polyphosphate or citrate. Examples include borax, sodium borate, sodium tetraborate, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium tripolyphosphate, sodium pentapolyphosphate and sodium citrate. They are used especially in amounts of from 0.1 to 3 % by weight, preferably from 0.1 to 1 % by weight, based on the total weight of the ink, in order to establish a pH value of e.g. from 4 to 9, especially from 5 to 8.5.

As further additives, the inks may comprise surfactants or humectants.

As surfactants there come into consideration the commercially available anionic or non-ionic surfactants. Suitable humectants in the inks according to the invention include, for example, urea or a mixture of sodium lactate (advantageously in the form of a 50 to 60 % aqueous solution) and glycerol and/or propylene glycol in amounts of preferably from 0.1 to 30 % by weight, especially from 2 to 30 % by weight.

Furthermore, the inks may also comprise customary additives, for example preservatives (such as glutaric dialdehyde and/or tetramethylolacetyleneurea), anti-oxidants, degassers/defoamers, viscosity regulators, flow improvers, anti-settling agents, gloss improvers, lubricants, adhesion promoters, anti-skin agents, matting agents, emulsifiers, stabilisers, hydrophobic agents, light stabilisers, handle improvers and anti-statics. Such agents are usually used in amounts of from 0.01 to 1 % by weight, based on the total weight of the ink.

The inks can be prepared in customary manner by mixing together the individual constituents in the desired amount of water.

The inks according to the invention are especially suitable for use in recording systems of the kind in which an ink is expressed from a small opening in the form of droplets which are directed towards a substrate on which an image is formed. Suitable substrates are, for example, paper, textile fibre materials, metal foils or plastics foils. Suitable recording systems are e.g. commercially available ink-jet printers for use in paper or textile printing.

Depending upon the nature of the use, it may be necessary for e.g. the viscosity or other physical properties of the ink, especially those properties which influence the affinity of the ink for the substrate in question, to be adapted accordingly.

In ink-jet printing, individual droplets of ink are sprayed onto a substrate in a controlled manner from a nozzle. For this purpose, predominantly the continuous ink-jet method and the drop-on-demand method are used. In the continuous ink-jet method, the droplets are produced continuously and any droplets not required for the printing are conveyed to a collecting vessel and recycled. In the drop-on-demand method, however, droplets are produced and printed as required; that is to say droplets are produced only when required for the printing. The production of the droplets can be effected, for example, by means of a piezo-inkjet head or by means of thermal energy (bubble jet).

The subsequent curing of the binder, that is to say the fixing of the print, can be effected in customary manner with the aid of heat or high-energy radiation. For this purpose, the print is irradiated either with electrons under an inert gas atmosphere (e.g. nitrogen) (electron beam curing) or with high-energy electromagnetic radiation, preferably in a wavelength

range of from 220 to 450 nm. In such a procedure, the chosen light intensities should be matched to the curing speed in order to avoid decomposition of the indicator.

When ink-jet printing is used, the procedure is advantageously as follows:

In Step a), a time-temperature integrator comprising at least one reversible indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined above, is applied by means of ink-jet printing to the substrate, especially to the packaging of ageing- and temperature-sensitive products or to labels that are applied to the packaging.

In a preferred embodiment, in Step a) it is possible additionally to apply, by means of ink-jet printing, a reference scale which reproduces the change in the colour of the indicator as a function of time, and it is possible to apply, preferably in black ink, further text (or information), such as an expiry date, product identification, weight, contents *etc.*.

Step a) is followed by Step b), activation, especially photo-induced coloration of the reversible indicator. The photo-induced curing of the binder advantageously includes the photo-induced coloration of the reversible indicator.

If desired, following Step b), an irreversible photo-sensitive indicator can be applied as tamper-proofing in the form of a covering over the time-temperature integrator. Suitable irreversible indicators include, for example, pyrrole derivatives, such as 2-phenyl-di(2-pyrrole)methane. Such a material turns irreversibly red when it is exposed to UV light.

Step c) is followed by the application of a protector, especially a colour filter, which prevents renewed photo-induced coloration of the reversible indicator. In the case of UV-sensitive indicators, there come into consideration yellow filters which are permeable only to light having typical wavelengths of more than 430 nm. Advantageously the protective film, that is to say the colour filter, can likewise be applied by means of ink-jet printing.

By means of the reference scale printed with the time-temperature integrator, absolute determination of quality grades is possible. The time-temperature integrator and the reference scale are advantageously arranged on a light-coloured substrate in order to facilitate reading.

Suitable substrate materials are both inorganic and organic materials, preferably those known from conventional layer and packaging techniques. There may be mentioned by way of example polymers, glass, metals, paper, cardboard *etc.*

The substrate can simultaneously form the packaging material for the perishable products or it can be applied to the packaging material, for example in the form of a label.

For example, in Step a) a printing ink, a printing ink concentrate and/or an ink-jet ink comprising a time-temperature integrator described above can be applied to the packaging of ageing- and temperature-sensitive products in the form of a barcode. The time- and/or temperature-induced decoloration of the indicator is advantageously so adjusted that once the expiry date has been passed, the barcode can no longer be read by a scanner. Alternatively, the time- and/or temperature-dependent decoloration of the indicator can also bring about a change in the barcode such that it can still be read, but, on being read, the information relating to the expiry date is given.

A prerequisite for the above-described time- and/or temperature-dependent visualisation of a barcode is, however, that the application of the indicator and its activation by irradiation are followed by the application of a protector, e.g. a colour filter, which prevents renewed photo-induced coloration of the reversible indicator. In order to prevent undesirable tampering involving e.g. subsequent renewed activation of the indicator, it is advantageously possible, after Step b), additionally to apply an irreversible photosensitive indicator in the form of a covering over the time-temperature integrator. Any tampering involving subsequent irradiation of the indicator would then be indicated by such an additional, then irreversibly activated, photosensitive indicator.

In further applications, the method according to the invention allows counterfeit-proof marking of documents as originals in a variety of ways. For example, identification papers, passports, banknotes, cheques and share certificates can be marked as being originals. The method according to the invention can equally be used for creating counterfeit-proof product identification labels. The economic damage caused to the global economy by product piracy and counterfeit goods is immense. It is necessary particularly to prevent counterfeiting in the case of pharmaceutical products. The method according to the invention allows, for example, the counterfeit-proof marking of blister packs, so that it is possible to have a decisive effect in preventing inferior preparations being passed off as the original articles. There is extremely wide scope for use of the marking technology based on the method according to the

invention. In addition to the labelling of branded products for mass consumption in order to ensure effective brand protection it is also possible for high-value goods that are at risk of counterfeiting, such as banknotes and chip cards, to be rendered counterfeit-proof in a simple and easily automated manner at relatively low cost. In the case of goods that are especially affected by product piracy, such as automotive spare parts, toys and CDs, it could be possible, in addition, to achieve copy protection that has been unachievable hitherto.

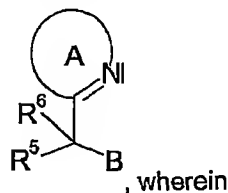
For example, a strip of a reversible indicator that is not visible under normal circumstances could be applied to a suitable substrate of a product or document to be protected against counterfeiting. Checking the authenticity of the article could then be effected very simply by irradiation (e.g. with a lamp that emits light of a suitable wavelength), so that the indicator strip would be visible to an observer or, in the event of a counterfeit, not visible to the observer. The authenticity of branded products could also be checked in this way. It might be possible for the reproduction of a mark on packaging to be so changed under the action of light of a certain intensity and/or a certain wavelength spectrum that a consumer would be in no doubt as to the origin of the goods. Limits will thus be set on brand and/or product piracy.

The above-described principle of counterfeit protection by means of the method according to the invention can also be used for protection against pirate copies, where the original is duplicated by irradiation with light using a copier, scanner *etc.* For example, a banknote could be provided with an invisible indicator strip which would become visible under the action of light during the copying operation and thus would clearly identify a copy as such. After a certain time period has elapsed, the indicator becomes invisible again so that the original is restored to its original state.

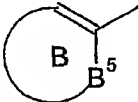
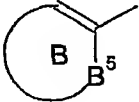
The invention accordingly relates also to a method for the counterfeit-proof labelling of products, which comprises the step of printing a time-temperature integrator as product label onto a product or onto the packaging of a product, wherein the time-temperature integrator comprises at least one indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined above, the product label being capable of being rendered visible by activation, especially by photo-induced coloration of the indicator.

Claims

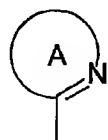
1. A method of printing a substrate, comprising
(a) printing onto the substrate a time-temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions.
2. A method according to claim 1, wherein
(b) the indicator is activated, especially by irradiation, after printing.
3. A method according to claim 2, wherein the indicator is a reversible indicator and
(c) after the activation of the reversible indicator there is applied a protector which prevents the photo-induced coloration of the reversible indicator.
4. A method according to any one of claims 1 to 3, wherein the substrate is a packaging material or a label applied to the packaging material.
5. A method according to any one of claims 1 to 4, wherein the transfer reactions are based on the transfer of charged or uncharged hydrogen atoms or hydrogen isotopes.
6. A method according to any one of claims 1 to 5, wherein the reversible indicator is a compound of the general formula



B is an electron-attracting group, which is preferably selected from the group consisting of a nitrile group, an ester group ($-\text{C}(=\text{O})\text{OEt}$), a carboxylic acid group, an aldehyde group ($-\text{C}(=\text{O})\text{H}$), a keto group, a fully or partially halogenated alkyl radical, preferably a trifluoromethyl group, a halogen atom, a nitro group, $-\text{PPh}_3^+ \text{X}^-$, wherein X^- is an anion, preferably Cl^- ; and wherein

B is a radical , the radical  being a $\text{C}_6\text{-C}_{30}$ aryl radical or $\text{C}_2\text{-C}_{30}$ heteroaryl radical, which can be unsubstituted or substituted; and wherein

B⁵ is a nitrogen atom or a group C-R¹¹ and R¹¹ is a nitro group, a cyano group, a carboxylic acid group or a derivative thereof, such as a carboxylic acid ester group or a carboxylic acid amide group, a ketone group or an aldehyde group; and wherein

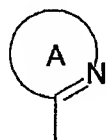


the radical is a C₂-C₃₀ heteroaryl radical, which can be unsubstituted or substituted; and wherein

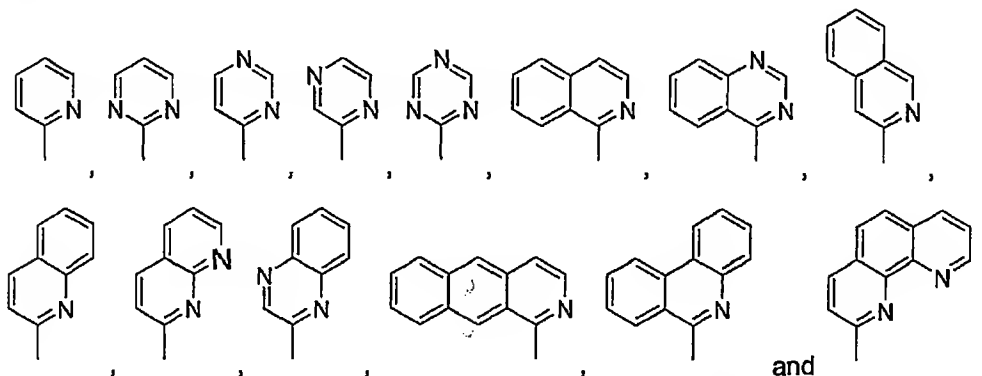
R⁵ is a hydrogen atom, an isotope D or T thereof, a nitrile group, an ester group, an aldehyde group, a carboxylic acid group, a keto group, a fluorine atom, a chlorine atom, a bromine atom or a C₁₋₁₈alkyl radical, preferably a C₁₋₄alkyl radical, a C₆-C₁₄aryl radical, preferably an unsubstituted or substituted phenyl group, or a C₂-C₁₃heteroaryl radical, preferably an unsubstituted or substituted pyridine group; and wherein

R⁶ is a hydrogen atom (H) or an isotope thereof (D or T).

7. A method according to claim 6, wherein



the radical is selected from the group consisting of:

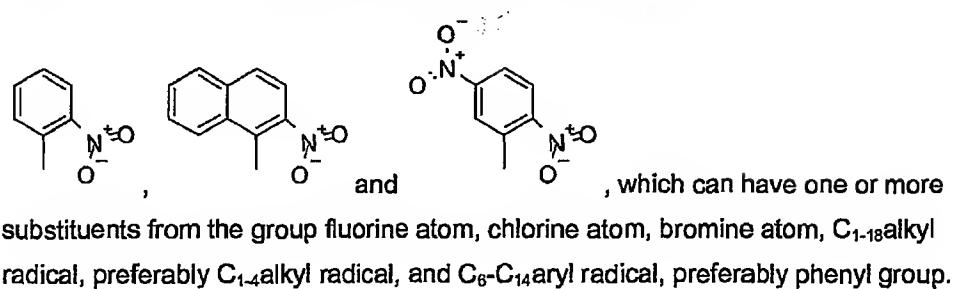


which can have one or more substituents from the group fluorine atom, chlorine atom, bromine atom, C₁₋₁₈alkyl radical, preferably C₁₋₄alkyl radical, and C₆-C₁₄aryl radical, preferably phenyl group.

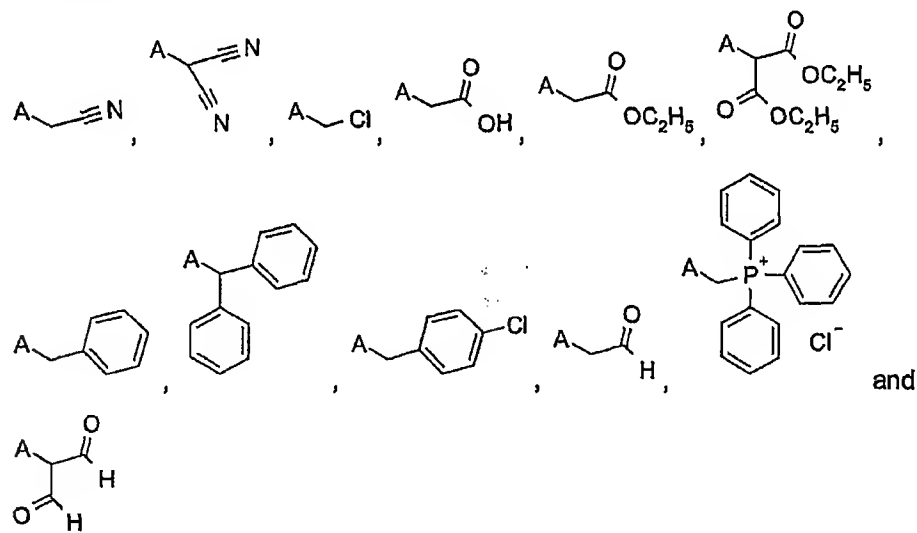
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8. A method according to claim 6, wherein the

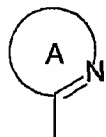
radical  is selected from the group consisting of:



9. A method according to claim 6, wherein the radical B is selected from the group consisting of:

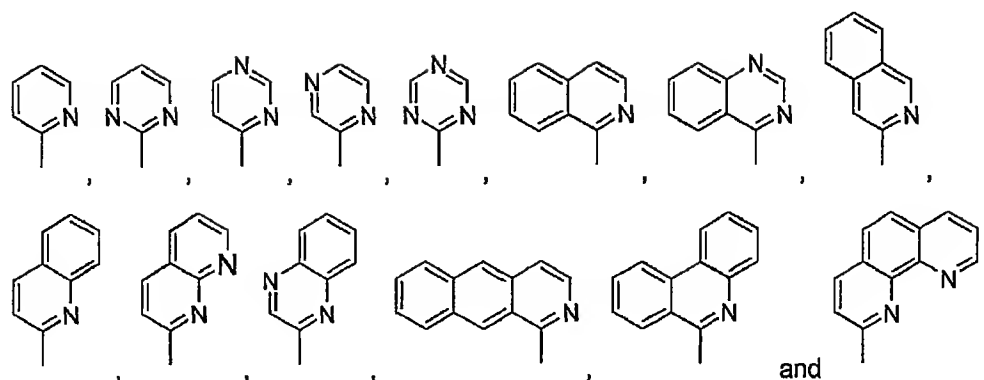


10. A method according to claim 9, wherein A is the radical

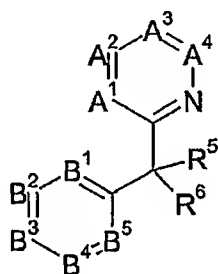


selected from the group consisting of:

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11. A method according to any one of claims 1 to 10, wherein the reversible indicator is a compound of general formula



(I), wherein

A¹ is a nitrogen atom or a group C-R¹,

A² is a nitrogen atom or a group C-R²,

A³ is a nitrogen atom or a group C-R³,

A⁴ is a nitrogen atom or a group C-R⁴, wherein

R¹, R², R³ and R⁴ are each independently of the others a hydrogen atom, an isotope thereof or a fluorine atom, a chlorine atom, a bromine atom, a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, or a C₆-C₁₄aryl radical, especially a phenyl group,

R⁵ is a hydrogen atom, an isotope thereof (D or T), a nitrile group, an ester group, an aldehyde group, a carboxylic acid group, a keto group, a fluorine atom, a chlorine atom, a bromine atom or a C₁₋₁₈alkyl radical, especially a C₁₋₄alkyl radical, a C₆-C₁₄aryl radical, especially an unsubstituted or substituted phenyl group, or a C₂-C₁₃heteroaryl radical, especially an unsubstituted or substituted pyridine group,

R⁶ is a hydrogen atom (H) or an isotope thereof (D or T),

B¹ is a nitrogen atom or a group C-R⁷,

B² is a nitrogen atom or a group C-R⁸,

B³ is a nitrogen atom or a group C-R⁹,

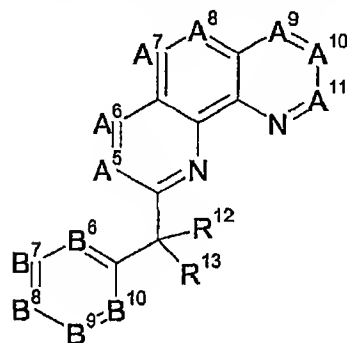
B⁴ is a nitrogen atom or a group C-R¹⁰,

B⁵ is a nitrogen atom or a group C-R¹¹, wherein

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R^7 , R^8 , R^9 and R^{10} are each independently of the others a hydrogen atom, an isotope thereof or a fluorine atom, a chlorine atom, a bromine atom or a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, or a C_6-C_{14} aryl radical, especially a phenyl group, and R^{11} is a nitro group, a cyano group, a carboxylic acid group or a derivative thereof, such as a carboxylic acid ester group or a carboxylic acid amide group, a ketone group or an aldehyde group;

a compound of general formula



(II), wherein

A^5 is a nitrogen atom or a group $C-R^{14}$,

A^6 is a nitrogen atom or a group $C-R^{15}$,

A^7 is a nitrogen atom or a group $C-R^{16}$,

A^8 is a nitrogen atom or a group $C-R^{17}$,

A^9 is a nitrogen atom or a group $C-R^{18}$,

A^{10} is a nitrogen atom or a group $C-R^{19}$,

A^{11} is a nitrogen atom or a group $C-R^{20}$, wherein

R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} and R^{20} are each independently of the others a hydrogen atom, an isotope thereof, a fluorine atom, a chlorine atom, a bromine atom, a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, or a C_6-C_{14} aryl radical, especially a phenyl group, R^{12} is a hydrogen atom, an isotope thereof (D or T), a nitrile group, an ester group, an aldehyde group, a carboxylic acid group, a keto group, a fluorine atom, a chlorine atom, a bromine atom or a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, a C_6-C_{14} aryl radical, especially an unsubstituted or substituted phenyl group, or a C_2-C_{13} heteroaryl radical, especially an unsubstituted or substituted pyridine group,

R^{13} is a hydrogen atom (H) or an isotope thereof (D or T),

B^6 is a group $C-R^{21}$,

B^7 is a group $C-R^{22}$,

B^8 is a group $C-R^{23}$,

B^9 is a group $C-R^{24}$,

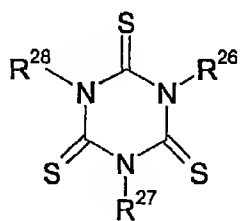
B^{10} is a group $C-R^{25}$, wherein

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R^{21} , R^{22} , R^{23} and R^{24} are each independently of the others a hydrogen atom, an isotope thereof or a fluorine atom, a chlorine atom, a bromine atom or a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, or a C_6-C_{14} aryl radical, especially a phenyl group, and

R^{25} is a nitro group, a cyano group, a carboxylic acid group or a derivative thereof, such as a carboxylic acid ester group or a carboxylic acid amide group, a ketone group or an aldehyde group;

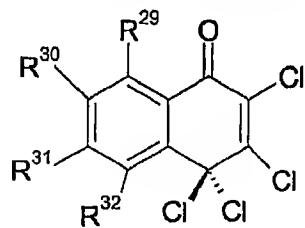
a compound of general formula



(III), wherein

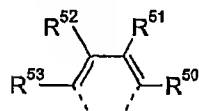
R^{26} , R^{27} and R^{28} are each independently of the others a C_{1-8} alkyl radical, especially a methyl or ethyl group;

a compound of general formula



(IV), wherein

R^{29} , R^{30} , R^{31} and R^{32} are each independently of the others a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, a C_{1-18} alkyl radical, especially a C_{1-4} alkyl radical, or a C_6-C_{14} aryl radical, especially a phenyl group, or two of the radicals R^{29} , R^{30} , R^{31} and R^{32} together form a group of the formula

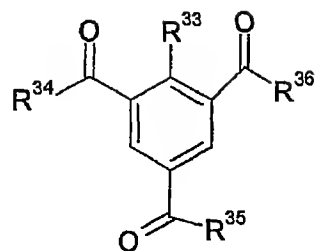


, wherein

R^{50} , R^{51} , R^{52} and R^{53} are each independently of the others H, a C_1-C_{18} alkyl radical or a C_6-C_{18} aryl radical, which can be unsubstituted or substituted;

a compound of general formula

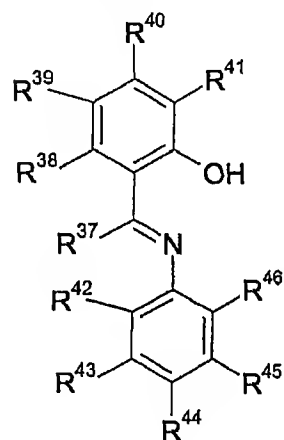
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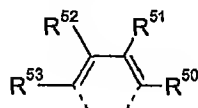
(V), wherein

 R^{33} is a C_{1-18} alkyl radical, R^{34} , R^{35} and R^{36} are each independently of the others a hydrogen atom or a C_{1-18} alkyl radical; or

a compound of general formula



(VI), wherein

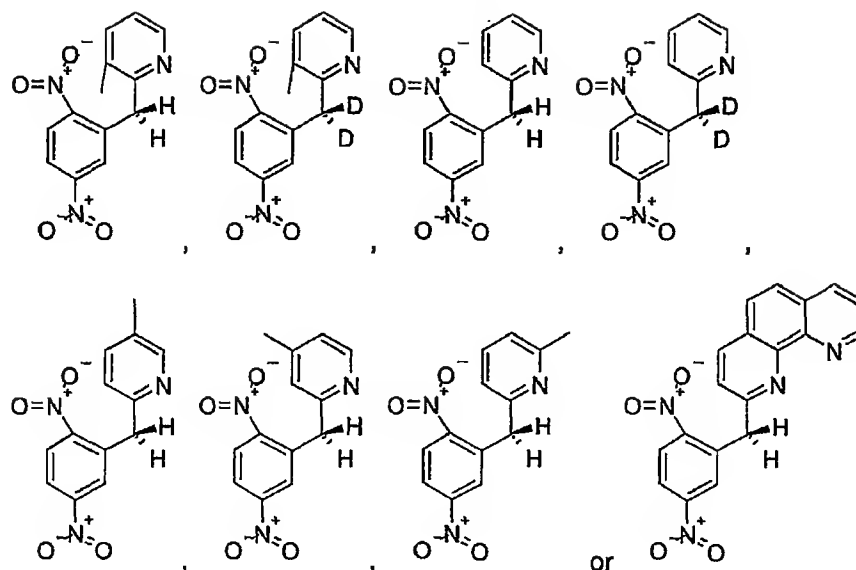
 R^{37} is a hydrogen atom or a C_{1-18} alkyl radical, and R^{38} , R^{39} , R^{40} , R^{41} , R^{42} , R^{43} , R^{44} , R^{45} and R^{46} are each independently of the others a hydrogen atom, a C_{1-18} alkyl radical or a C_{1-18} alkoxy radical, ortwo of the radicals R^{38} , R^{39} , R^{40} , R^{41} , R^{42} , R^{43} , R^{44} , R^{45} and R^{46} together form a group of the formula

, wherein

 R^{50} , R^{51} , R^{52} and R^{53} are each independently of the others H, a C_1 - C_{18} alkyl radical or a C_6 - C_{18} aryl radical, which can be unsubstituted or substituted.

12. A method according to claim 11, wherein the reversible indicator is a compound of general formula I or II, namely

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13. A printing ink or printing ink concentrate, comprising a time-temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined in claim 11.
14. An ink-jet ink, comprising a time-temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined in claim 11.
15. A printed substrate, obtainable in accordance with the process according to any one of claims 1 to 12.
16. A method of determining the quality of ageing- and temperature-sensitive products, which comprises the following steps:
 - a) printing onto a substrate a time-temperature integrator which comprises at least one indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined in claim 11,
 - b) activation, especially photo-induced coloration, of the indicator,
 - c) optionally application of a protector which prevents renewed photo-induced coloration of the indicator, and
 - d) determination of the degree of time- or temperature-induced decoloration and, taking account of the degree of decoloration, the quality of the product.

17. A method according to claim 16, wherein the quality of the product is determined by evaluating the degree of decoloration with the aid of a reference scale.
18. A method for the counterfeit-proof labelling of products, which comprises the following step:
 - a) printing a time-temperature integrator as product label onto a product or onto the packaging of a product, wherein the time-temperature integrator comprises at least one indicator having photochromic properties based on transfer reactions, especially a reversible indicator of formula I, II, III, IV, V or VI, as defined in claim 11, the product label being capable of being rendered visible by activation, especially by photo-induced coloration of the indicator.

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/EP2004/051733

A. CLASSIFICATION OF SUBJECT MATTER

 IPC 7 B41M3/14 C09D11/00 G01K3/04 G01K11/16 B41M7/00
 B65D79/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B41M C09D G01K B65D C09K G09F G01N G07D B42D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/39197 A (D.HAARER ET AL.) 5 August 1999 (1999-08-05) cited in the application page 1, line 8 - line 12 page 3, line 31 - page 4, line 6 page 5, line 23 - page 6, line 2 page 6, line 30 - page 9, line 33 claims 1-24; figures 1-3	1-18
X	EP 0 117 390 A (ALLIED CORPORATION) 5 September 1984 (1984-09-05) cited in the application claims 1,2; figure 5 page 3, line 19 - line 21 page 4, line 9 - line 24 page 5, line 7 - line 36 page 12, line 22 - line 25 page 13, line 37 - page 14, line 3	1-18
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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& document member of the same patent family

Date of the actual completion of the International search

26 October 2004

Date of mailing of the International search report

03/11/2004

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

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Bacon, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/051733

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 593 486 A (J.F.OLIVER ET AL.) 14 January 1997 (1997-01-14) column 1, line 6 - line 18 column 7, line 49 - column 8, line 11 column 12, line 4 - column 17, line 45 claims 1,5-8,11,12 -----	1-15,18
X	GB 2 272 861 A (UNIVERSITY COLLEGE CARDIFF CONSULTANTS LIMITED) 1 June 1994 (1994-06-01) claims 1-7; figures 1,2 page 1, line 1 - line 4 page 3, line 2 - page 4, line 29 -----	1-5, 13-15,18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/051733

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WO 9939197	A	05-08-1999	DE 19803208 A1	05-08-1999
			WO 9939197 A1	05-08-1999
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			JP 2002501862 T	22-01-2002
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